


Neutron scattering from Hydrogen in Metals and from hydrogen on Carbon nanotubes

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Why Neutron Scattering from Hydrogen?

- ◆ Large incoherent scattering cross section of H makes it easy to detect
 - ◆ Useful coherent cross section of Deuterium to extract pairwise correlations
 - ◆ Mixing H and D gives variable scattering density from negative (H) to positive (D)
 - ◆ Small proton mass gives strong inelastic scattering
 - ◆ Ideal technique for testing ab initio (Density Functional) modelling methods
 - ◆ Scattering from ortho and para-hydrogen molecules is dramatically different (Young and Koppel *Phys Rev A* 135 (1964) 603))
 - ◆ Position uncertainty of proton wave function is large but easily measured with neutron scattering
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Hydrogen Energy Needs Hydrogen Storage: **Target 7% by Weight**

- ◆ Greenhouse warming requires reduction of CO₂ emissions
- ◆ Limit to oil supplies (outside Middle East)
- ◆ **Implies Hydrogen Energy!!**
- ◆ Use of hydrogen for transport implies hydrogen storage on-board vehicle
- ◆ Possible Hydrogen Storage Methods
 - (a) High pressure hydrogen (350 Bars?)
 - (b) Liquid hydrogen (BMW!)
 - (c) Intermetallic hydride stores
 - (d) H₂ molecules on SWNTs or other porous material

Physics of Hydrogen in Metals

◆ Different kinds of Binding

- H^+ + electron into a d-band metal with variable valency
 - extra electrons at the Fermi Surface – screens the H^+
- $H^- + M^+$ (alkali or alkali-earth metal giving ionic hydride)
- H covalently bonded as in $[AlH_4^-]$

H^+ is apparently best for hydrogen storage because:

It is mobile in the metallic host,

It sits on inter-metallic sites over a range of concentrations without changing the metal lattice

It can be reversibly added and removed.

But the known inter-metallic hosts are too heavy for use in cars

Quantum Properties of Hydrogen

- ◆ Because H is the lightest nucleus, its quantum properties are the most significant of all elements (Simple Harmonic Oscillator)
- ◆ Have to calculate the proton wave-function in the potential energy surface from total energy calculations (Zone Centre)
- ◆ Modelling has to allow for the zero point energy of H and the lower value of this for D
- ◆ Optimise lattice parameter to minimise the sum of the lattice energy and the zero point energy (i.e. smaller for D)
- ◆ See PRL 84 (2000) 1531

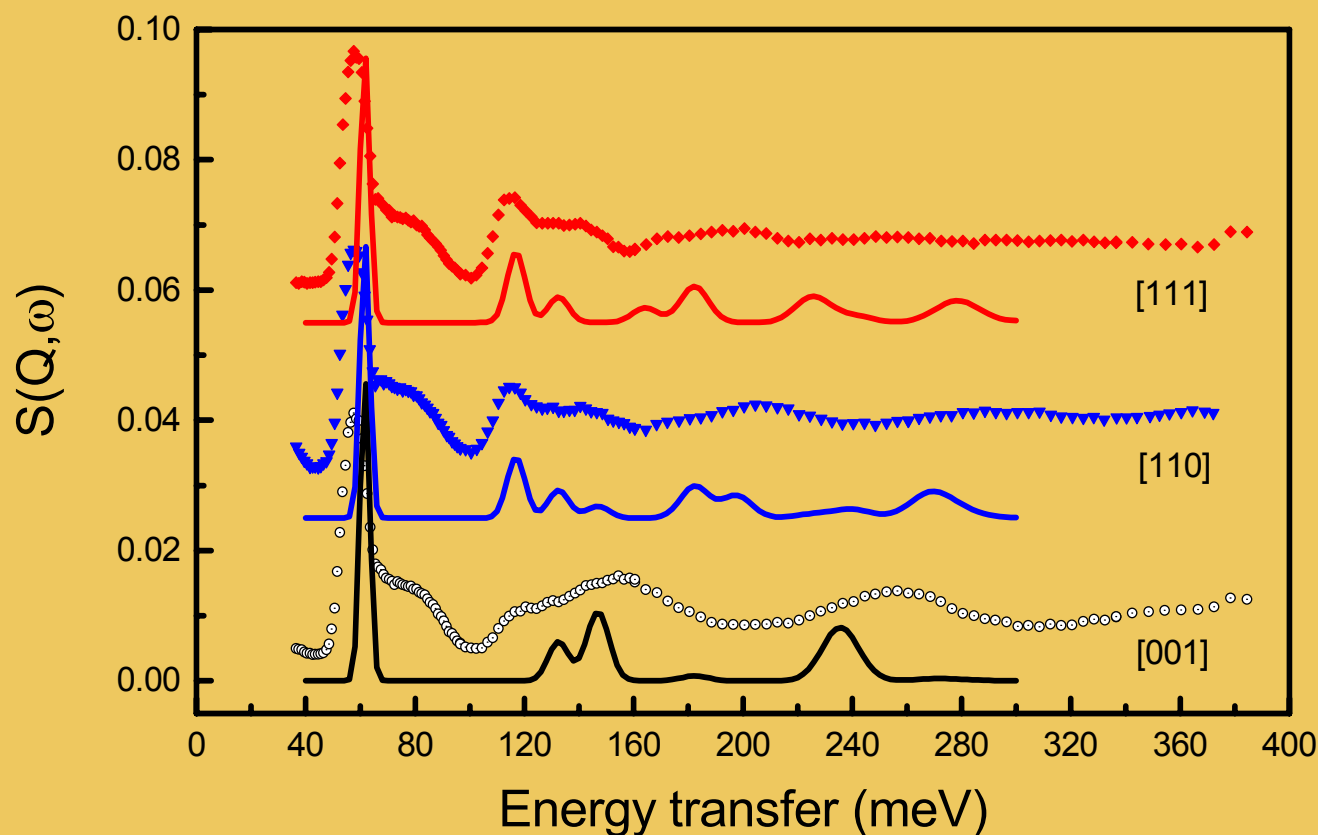
Classic Case: Hydrogen in Palladium

Produced as single crystals in β -phase

- ◆ Ab initio calculations for Zone Centre Phonon using Density Functional Theory (following Elsaesser)
- ◆ Calculate Energy surface seen by proton (very anharmonic, octahedral site more stable than tetrahedral)
- ◆ Calculate proton wave-functions
- ◆ In Cartesian functions
 - ◆ -Ground state is (0,0,0)
 - ◆ 1st Excited State is (1,0,0)
 - ◆ 2nd levels include (1,1,0) 3 degenerate states; (2,0,0) (resolved into two degenerate states and a singlet by anharmonicity)

IINS from H in Pd Single Crystal

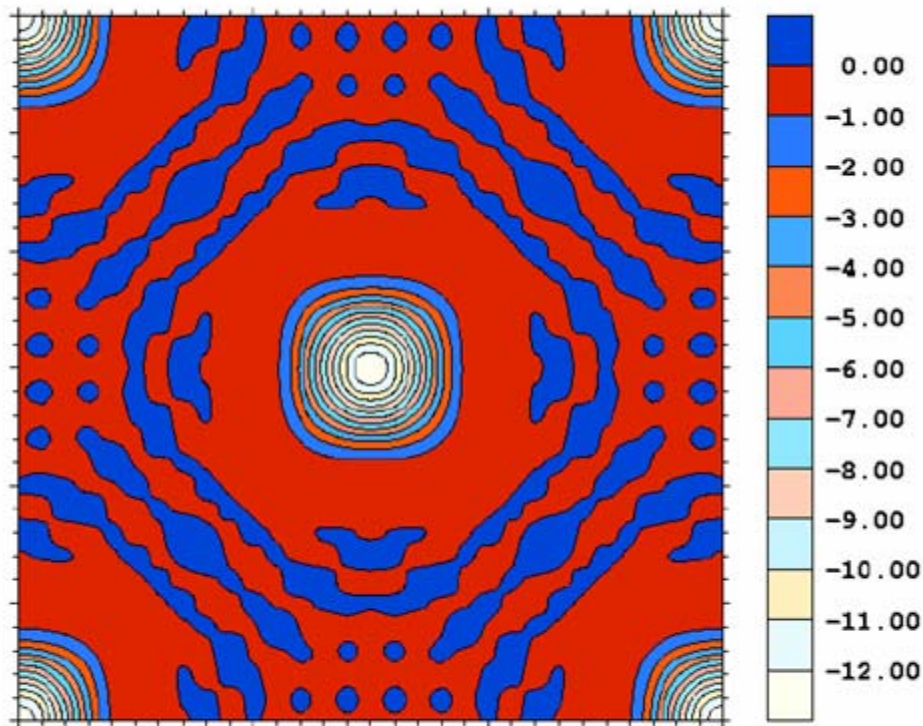
IN1b at ILL – spectra in different Q directions
Calculations convoluted with resolution function



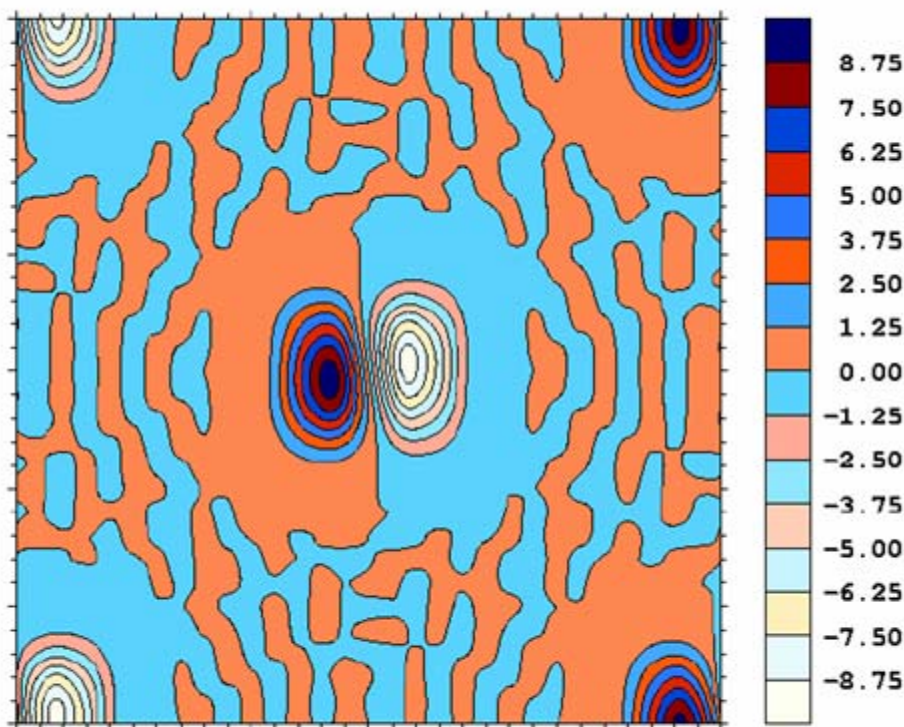
Energy Levels – Calculated and measured

| <i>Energy state</i> | <i>Theory (meV)</i> | <i>PdH_{1.0} (meV)</i> | <i>PdH_{0.85} (meV)</i> |
|---|-------------------------|------------------------------------|-------------------------------------|
| $e_{1, 001\rangle} = e_{1, 010\rangle} = e_{1, 100\rangle}$ | 62 | 55.8 | 57 |
| $e_{2, 011\rangle} = e_{2, 101\rangle} = e_{2, 110\rangle}$ | 117 | 112 | 115.5 |
| $e_{2, C\rangle}$ | 132 | 135 | 139 ± 2 |
| $e_{2, A\rangle} = e_{2, B\rangle}$ | 147 | 148 | 155 ± 3 |
| $e_{3, 111\rangle}$ | 164 | - | ~ 170 |

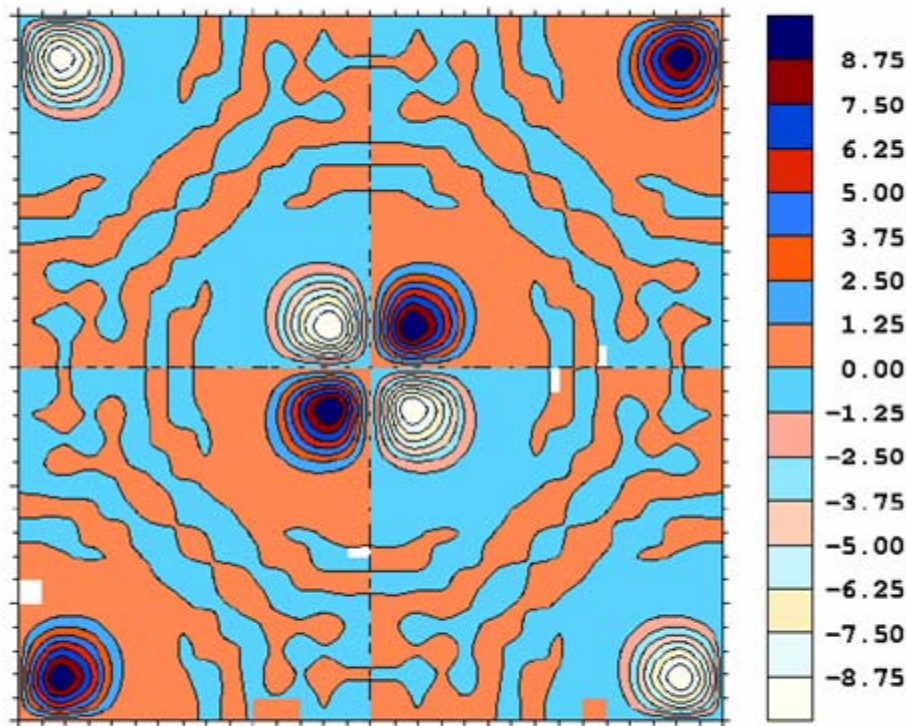
Ground state wave function of proton at mid plane of f.c.c. unit cell



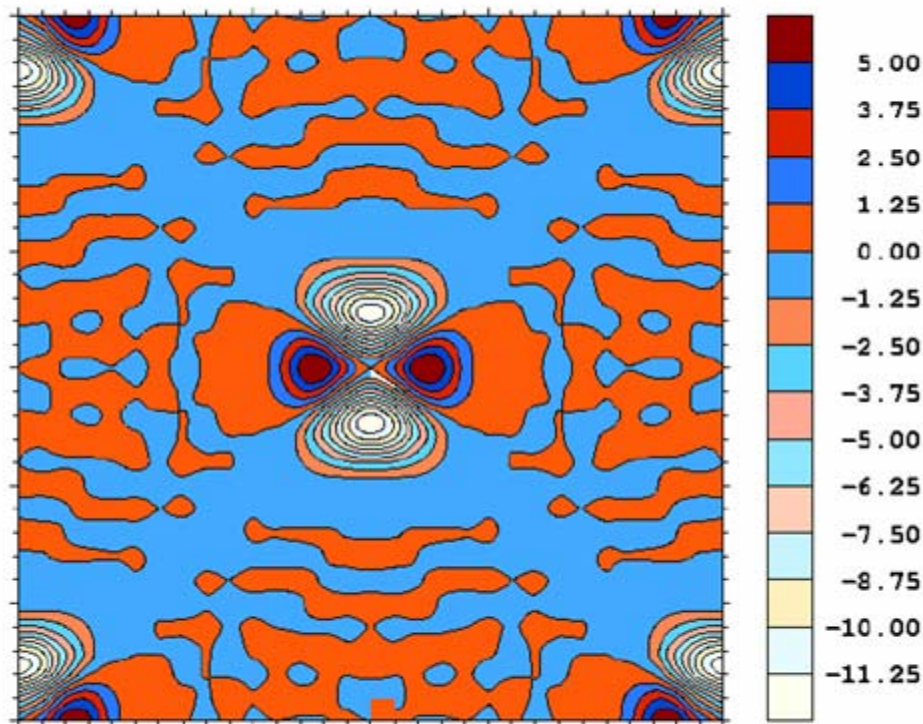
Wave function of proton for (100) level at octahedral site in Pd



Wave function for the (110) level of H in Pd at 117 meV (twice (100) level energy)



(200) $|A\rangle$ and (200) $|B\rangle$ wave functions for protons in Pd, corresponding to 147 meV (notation as for perturbation theory but perturbations from harmonic are too big, requiring Fourier fits)



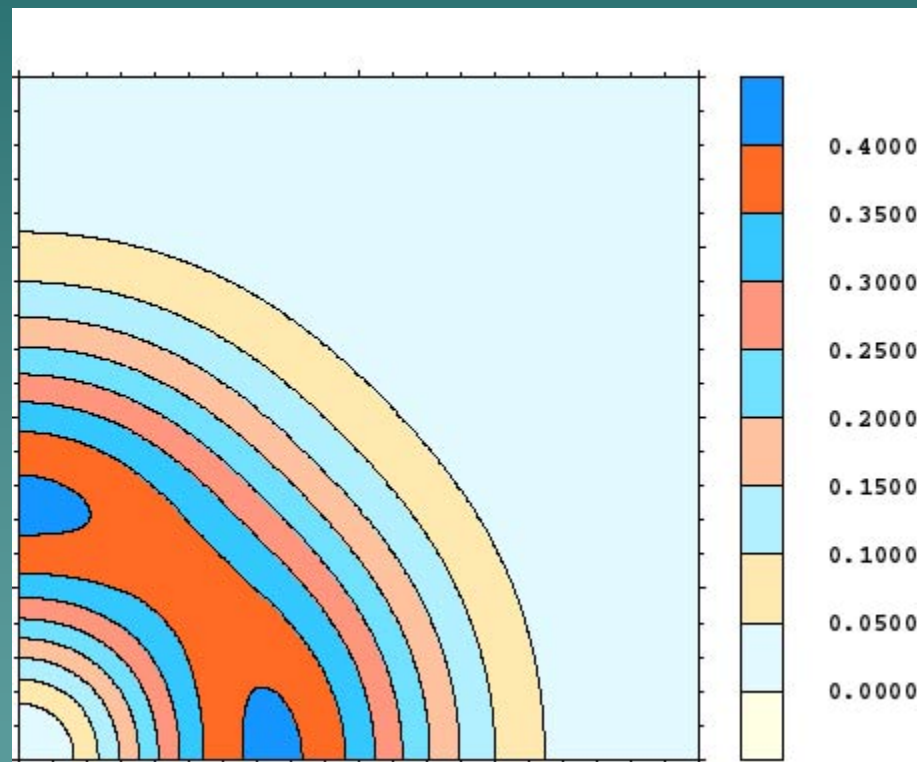
Calculations of IINS cross section

- ◆ We can obtain $d^2\sigma/d\omega dQ$ directly from the calculated wave functions using Fermi's Golden Rule

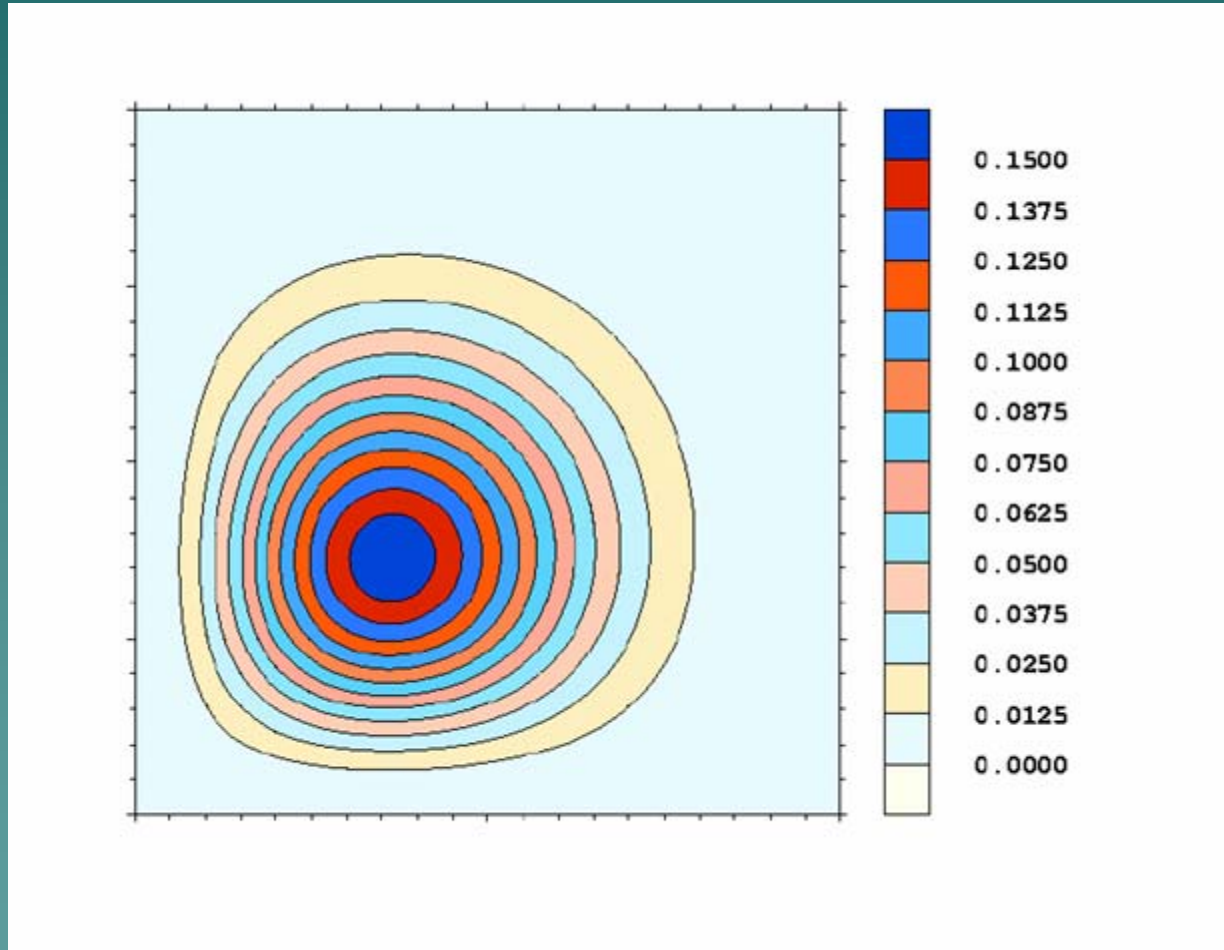
$$S_{inc}(\mathbf{Q}, \omega) = \sum_f \left| \int \phi_i(\mathbf{r}) \exp(-i \mathbf{Q} \cdot \mathbf{r}) \phi_f(\mathbf{r}) d\mathbf{r} \right|^2 \cdot \delta(\varepsilon_f - \varepsilon_i + \hbar\omega)$$

Here i and f refer to the initial and final wave functions

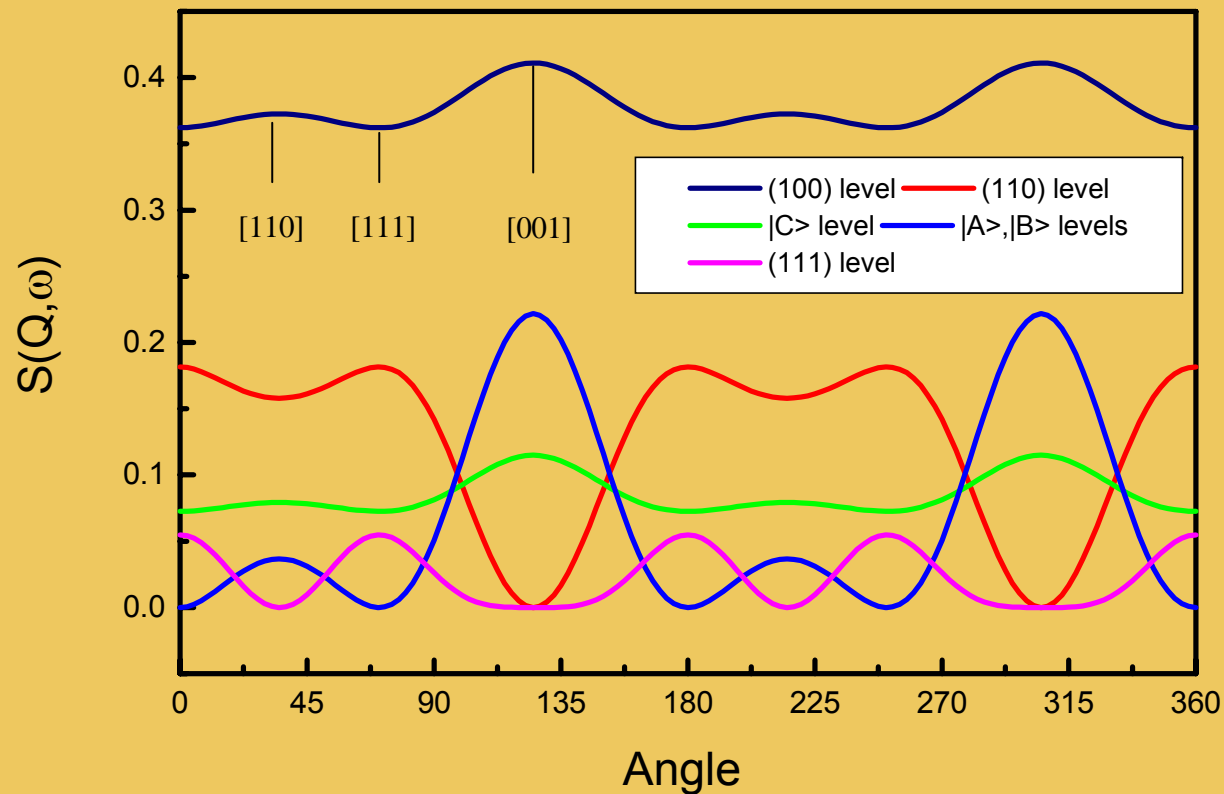
(Q_x, Q_y) quadrant of $S(Q, \omega)$ for the (100) energy level. This would be just $|Q|^2 \exp(-2W)$ in the harmonic approximation



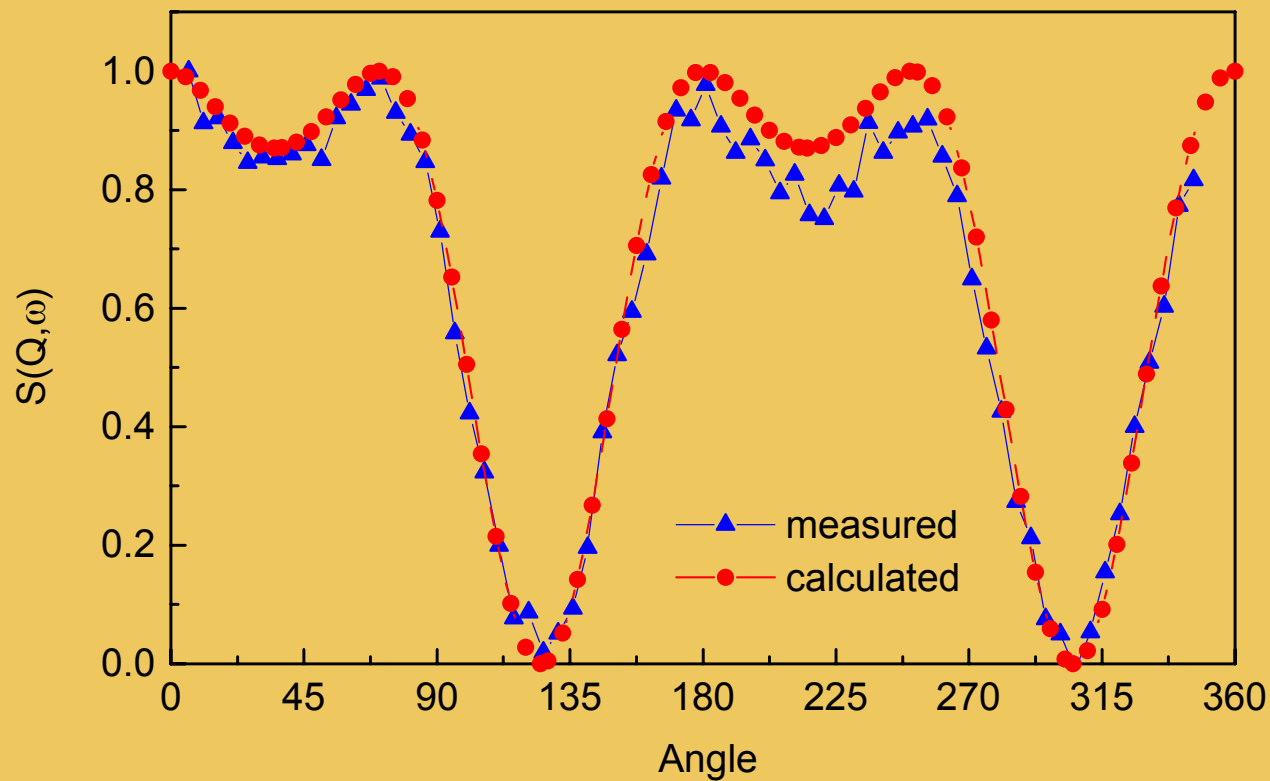
$S(Q, \omega)$ in $(+Q_x, +Q_y)$ quadrant for (110) level in PdH – note zero intensity in x,y directions because the excited state wave function is exactly antisymmetric in these directions



Intensity variation of $S(Q,\omega)$ as crystal is rotated about the (110) axis for different energy levels



Comparison of calculated intensity with experiment for the (110) level as a function of angle of rotation about the (110) axis. Note that the data has been corrected for background level chosen to optimise the fit



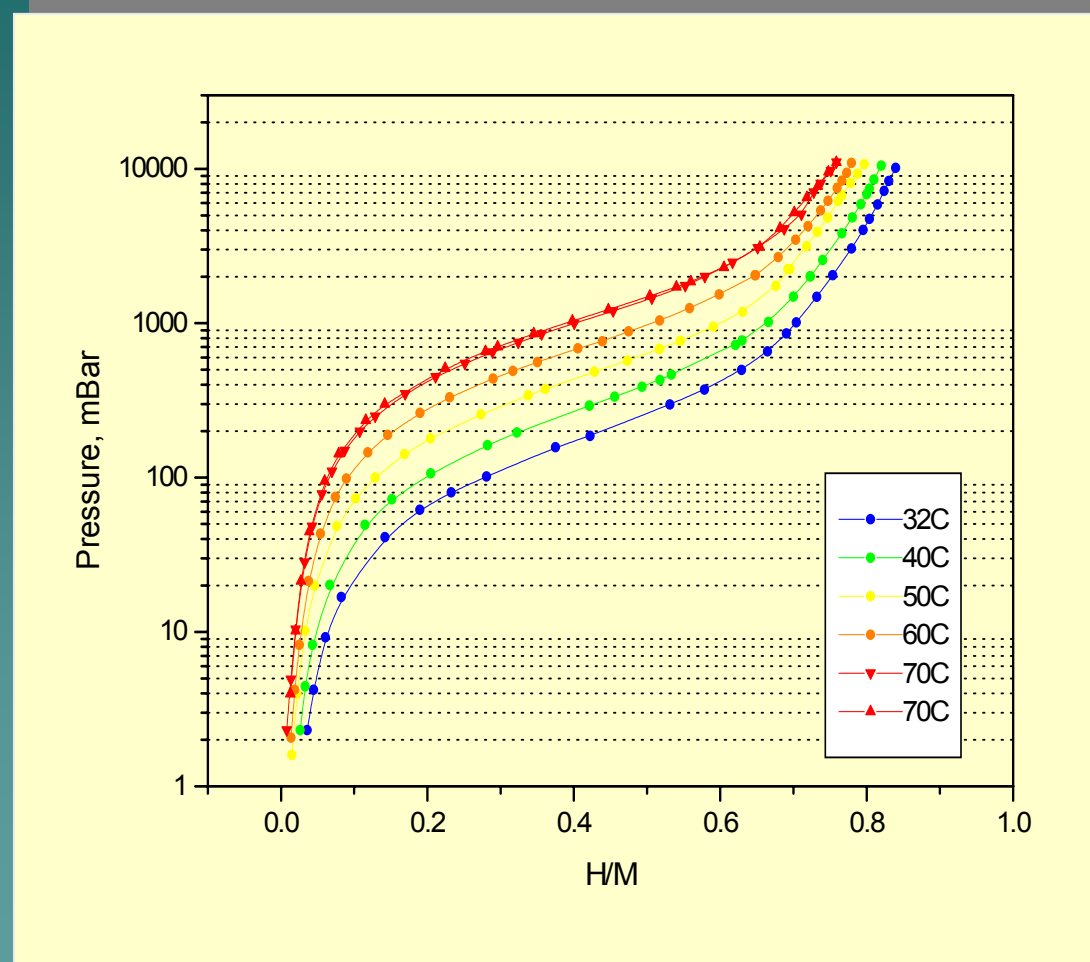
In Situ Studies of Hydrogen cycling in and out from hydride store

- ◆ Advantage of neutron scattering is that we can change the hydrogen content in situ by changing hydrogen pressures and temperatures
- ◆ Report here some measurements on two AB_5/H systems using OSIRIS diffractometer at ISIS
- ◆ Compounds have standard composition for metal hydride batteries but one is AB_5 and one is $AB_{4.8}$

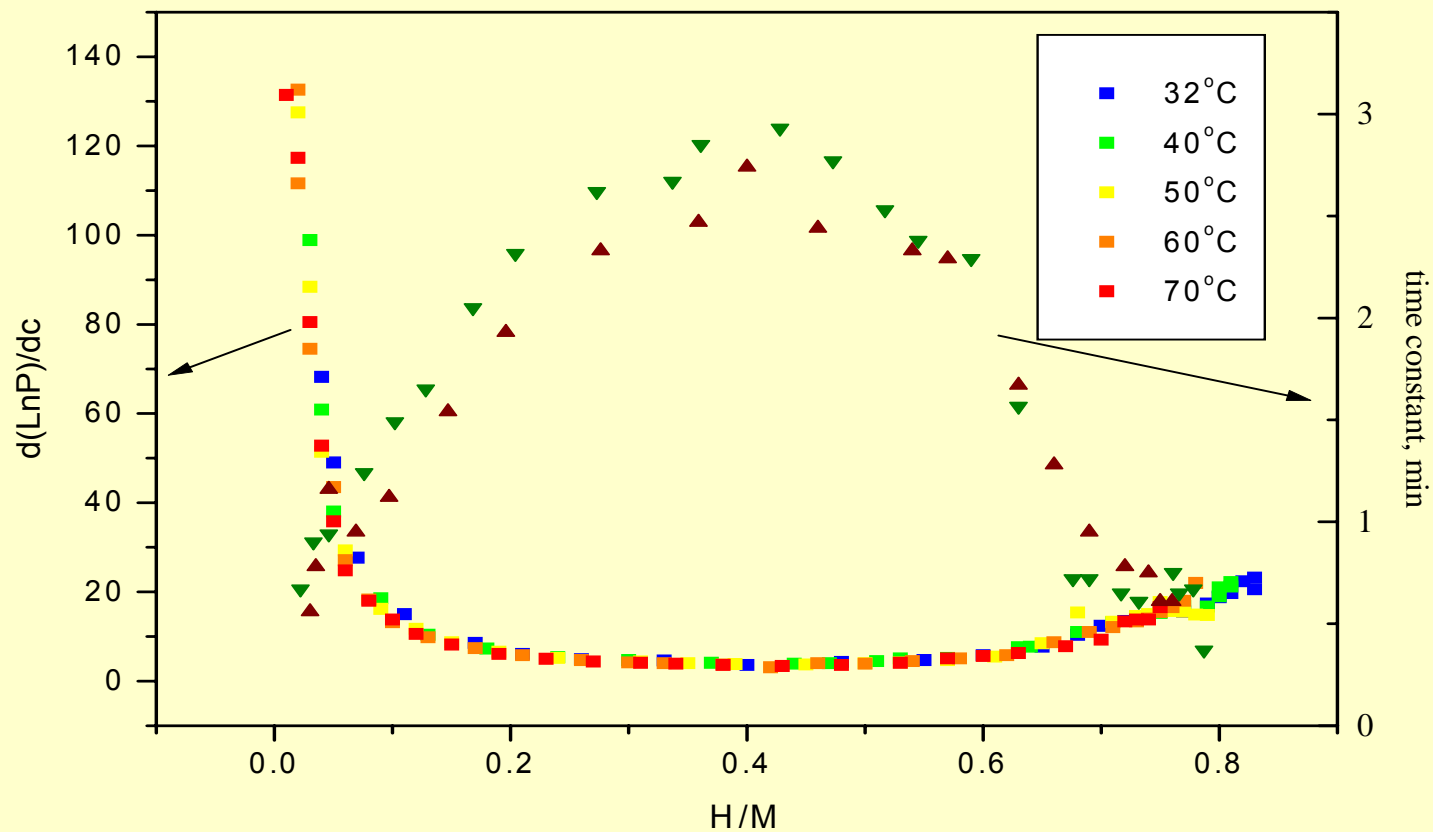
Isotherms measurements on metal hydride stores

- ◆ Ni Metal hydrides use AB_5 alloys based on $LaNi_5$ but use misch metal for La and contain significant quantities of 5 other elements
- ◆ Enormous improvements over $LaNi_5$ but took some 10 years of intensive effort
- ◆ Similar efforts will have to be made to develop workable light hydride compounds
- ◆ Breakthrough has been discovery of the effect of Ti in $NaAlH_4$ compounds

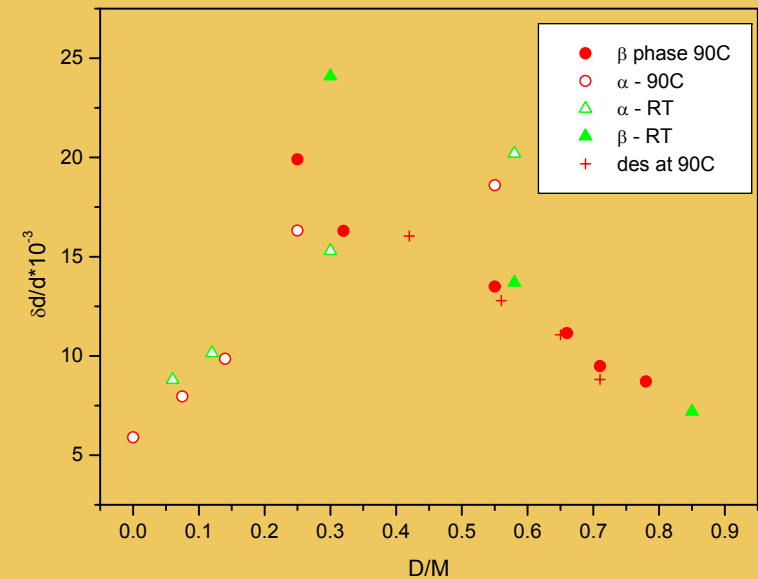
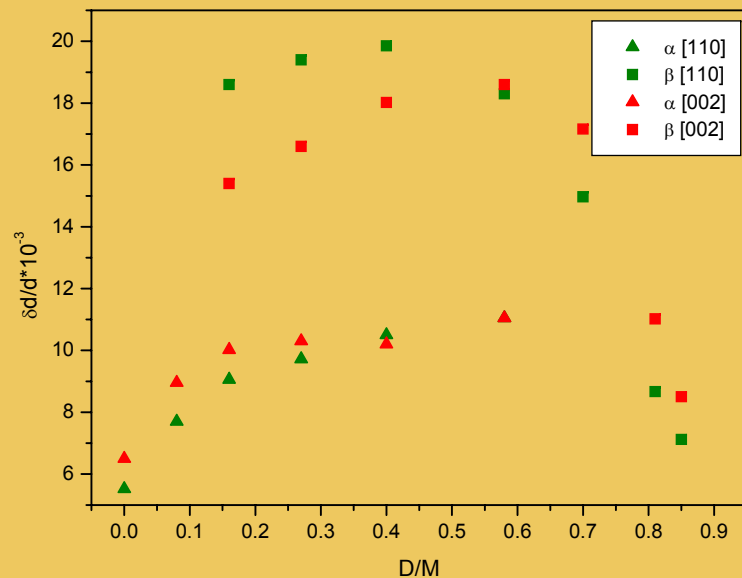
Set of isotherms measured for an $AB_{4.8}$ Alloy using the IGA computer-controlled microbalance



Comparison with $d\mu/dc$ with time constants for absorption measured with IGA. Time constants are large where $d\mu/dc$ is small



Line Broadenings measure local strain



Powder diffraction line broadening as a function of deuterium concentration (a) for AB_5 - and (b) for $AB_{4.8}$ - The instrumental contributions to the broadening have been subtracted. Note: alpha phase is not strained where it forms on the surface

IINS Studies of H₂ molecules adsorbed on Single Walled nanotube ropes at low temperatures

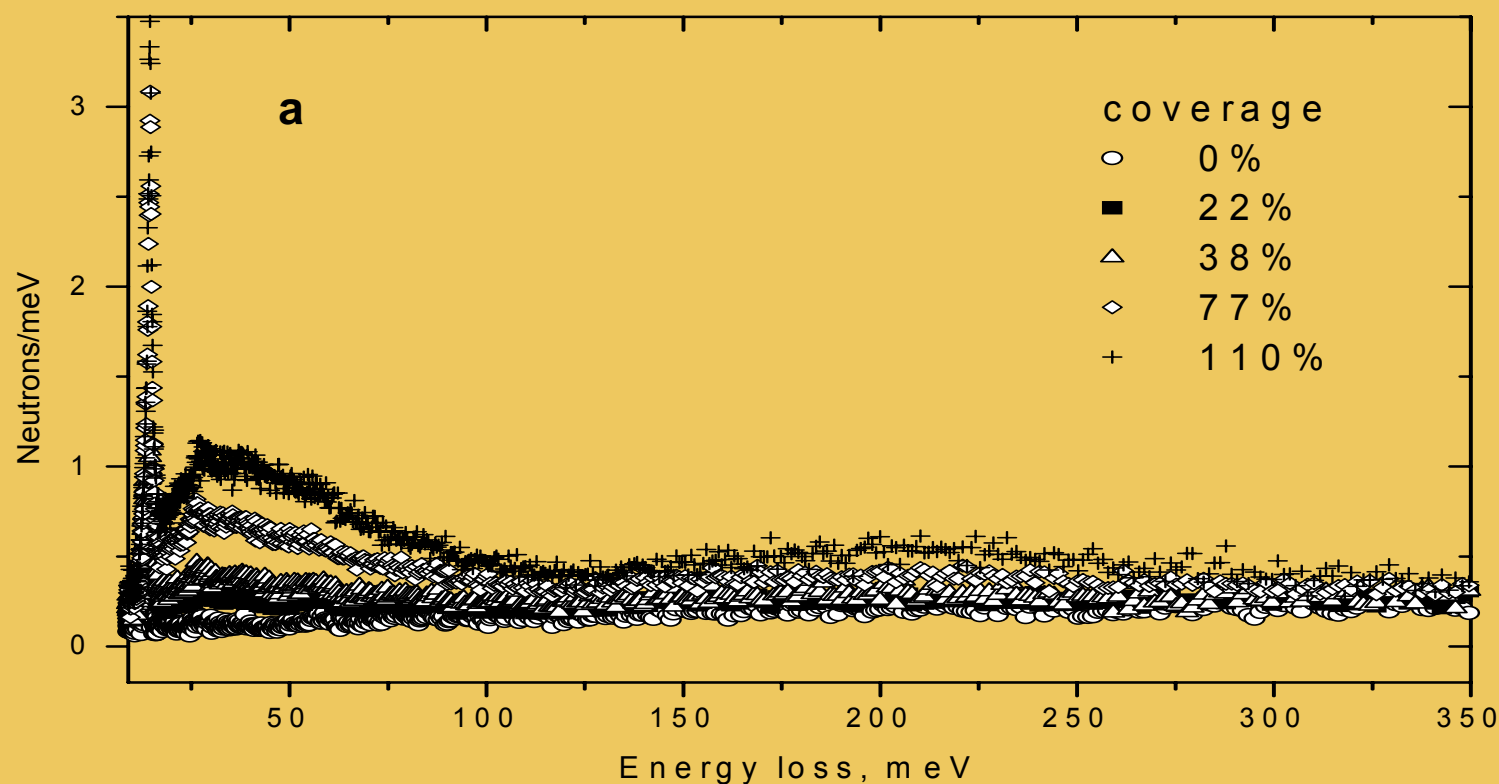
- ◆ Recent reports of large quantities of H₂ absorbed in carbon nanotubes at room temperature all seem to be spurious (water vapour?)
- ◆ However, physisorption on large surface area samples might store enough hydrogen at 80K and convenient pressures that might be more economical than liquid hydrogen at 20K.
- ◆ SWNTs offer high surface areas with geometries that might give stronger physi-sorption inside or between the tubes
- ◆ High resolution INS of the para-ortho, J=0 J=1 level cross-section provides an excellent method of analysing the different sites of physi-sorption

IINS Spectra from H₂ on SWNT for different H₂ coverages

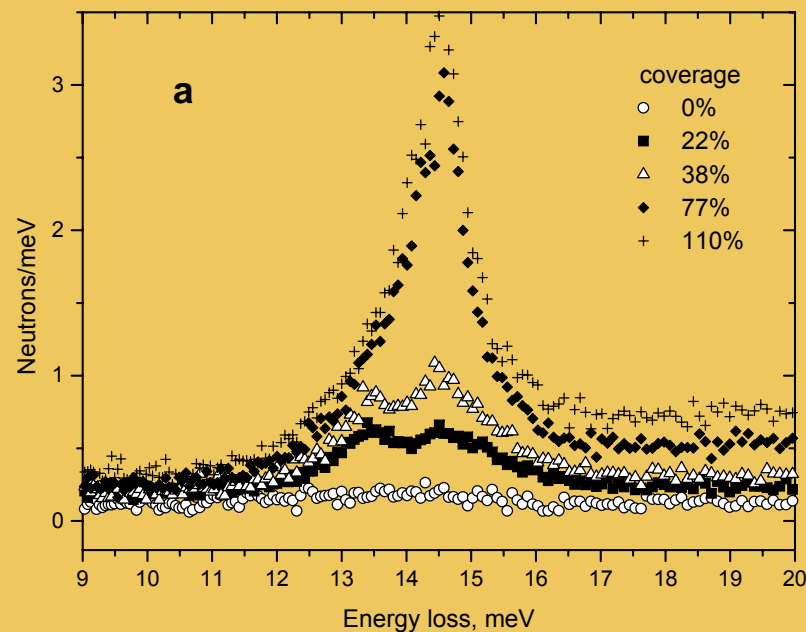
Sample is Carbolex (Selected grade) - Instrument is TOSCA at ISIS

Spectra for range of surface coverages

Sharp peak at 14.7 meV, no recoil – broad peaks at higher energy include recoil

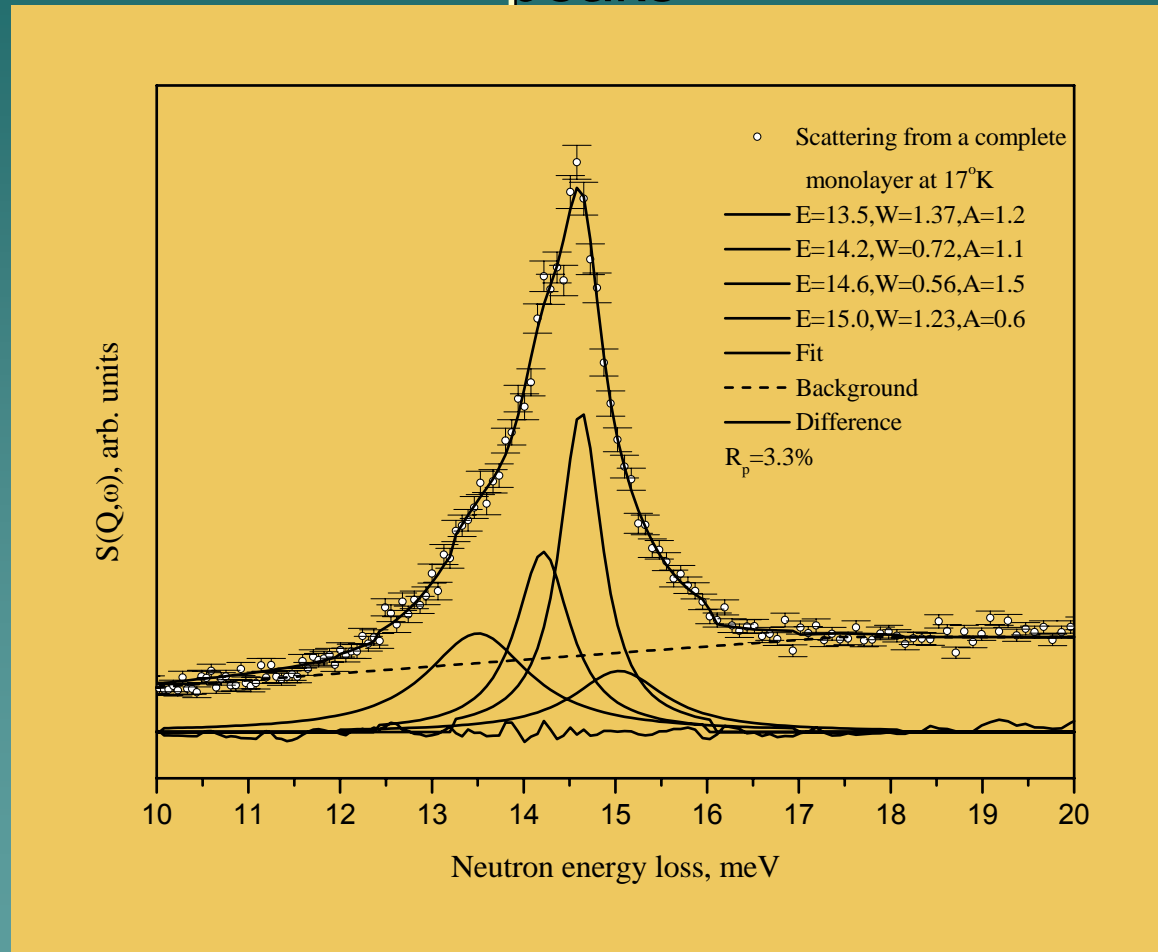


Detail in the 14.7 meV peak showing the development of the different peak components with increasing surface coverage. Note that the double peak structure dominates at lower coverages



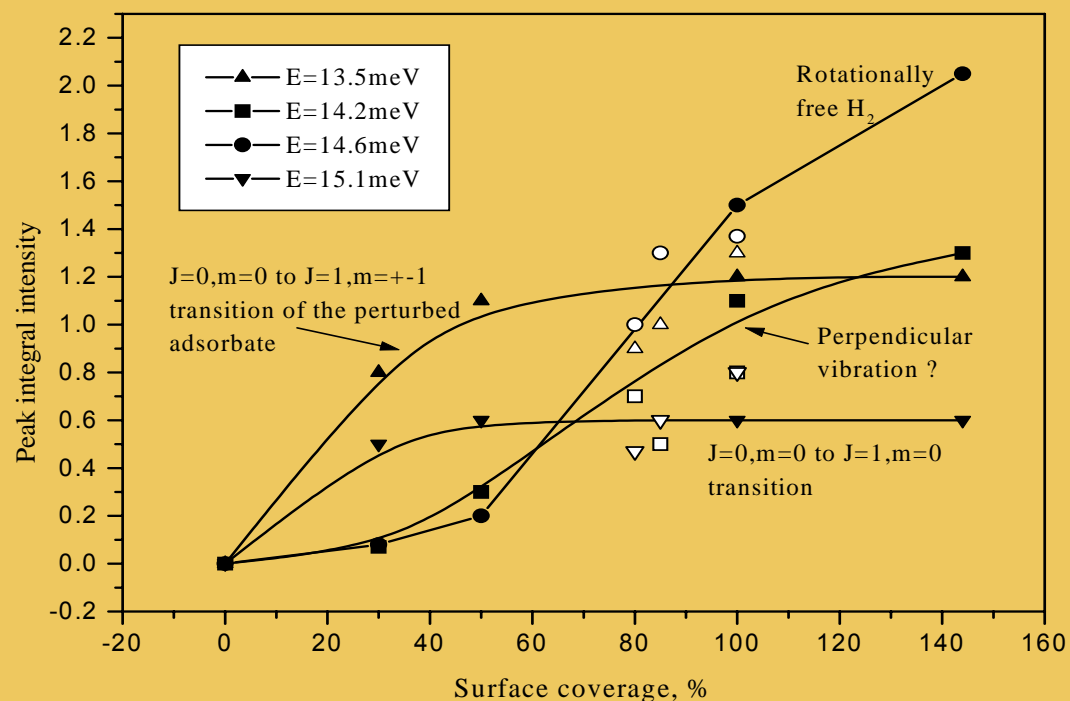
4 Gaussian fit to sample spectrum.

Free fits to the parameters show consistent mean energies and fixed 2:1 intensity ratio between 13.5 and 15.1 meV peaks



Variation of peak intensities as a function of surface coverage

2:1 peak intensity ratio suggests asymmetric site, i.e. vdW potential normal to planar surface. The $m = \pm 1$ states are at a lower average potential energy than the $m=0$ level where the molecule precesses with the defined axis of spin parallel to the surface.



Origin of 14.2 meV and 14.6 meV peaks

The origins of the 14.2 meV and the 14.6 meV peaks are illuminated by subsequent measurements on graphitic surfaces – we observe almost the same peaks – but it is clear that the 14.2 peak only appears when the first layer is complete - suggests that:

- (a) Both peaks referred to here are from H₂ on the convex surface of the nanotubes -
- (b) The 14.2 meV peak is due to a surface molecule that is covered by a molecule in the second layer.
- (c) The 14.6 meV peak is due to molecules in the second layer

Origin of the 13.8meV and 15.0 meV peaks

- ◆ Peaks appear together and grow in the same way with H₂ coverage so probably due to one type of site
- ◆ Area of 13.8 meV peak is nearly twice the area of 15.0 meV peak so can assume due to splitting in J=1 peak, i.e. the m=+/-1 (doublet) and the m=0 (singlet) states.
- ◆ Perhaps due to sites along the groove?
- ◆ Note: Adsorption measurements show the split site to have an adsorption energy of 75Kcal i.e about twice the value for the normal graphite surface.

Why are the energies reduced?

- Peak should be at 14.7 meV for free molecule
- First Order Perturbation Theory suggests mean energy should be unchanged but is about 14.3 meV
- Surface site peaks also reduced – Why??
- Due to difference in zero point energy for para and ortho ground states (Fitzgerald et al – C₆₀)?
- Or due to change in $d_{\text{H-H}}$ - the proton-proton distance - (due to shift in electron density from between the protons or actual charge transfer to nanotubes)?

Young and Koppel Expression

◆ $S_{J-J'}(Q, \omega) =$

$$\sum_{Jm, J'm'} F_{Jm, J'm'}(Q) \delta(\omega - \omega_{mJ, m'J'}) * S_{CM}(Q, \omega)$$

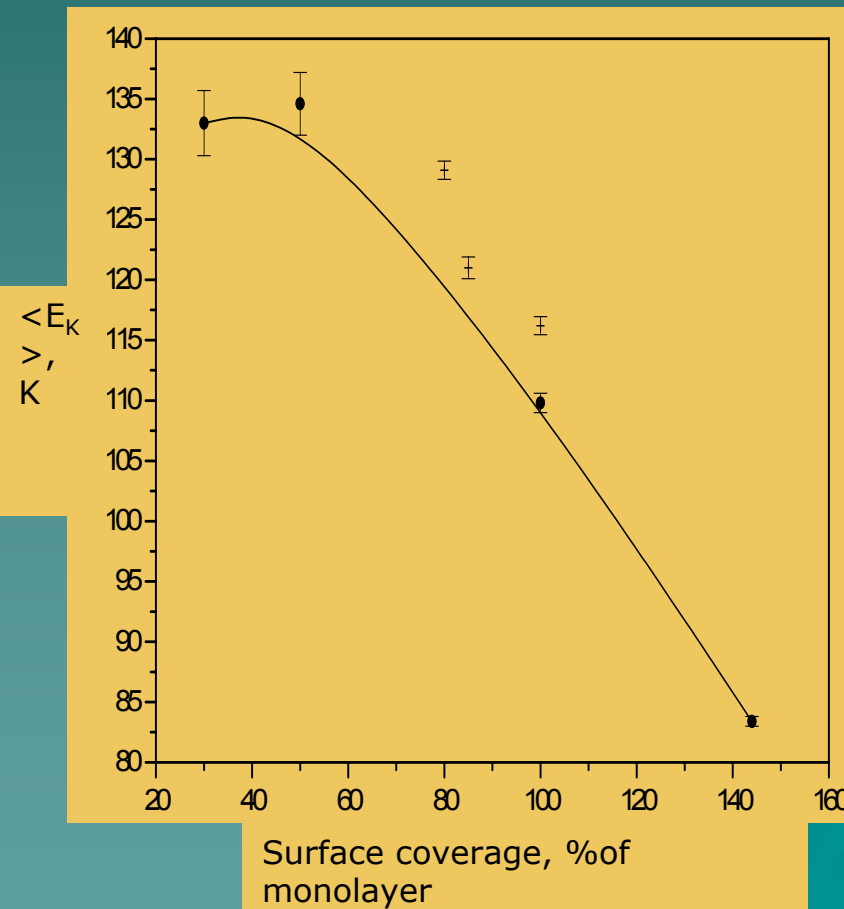
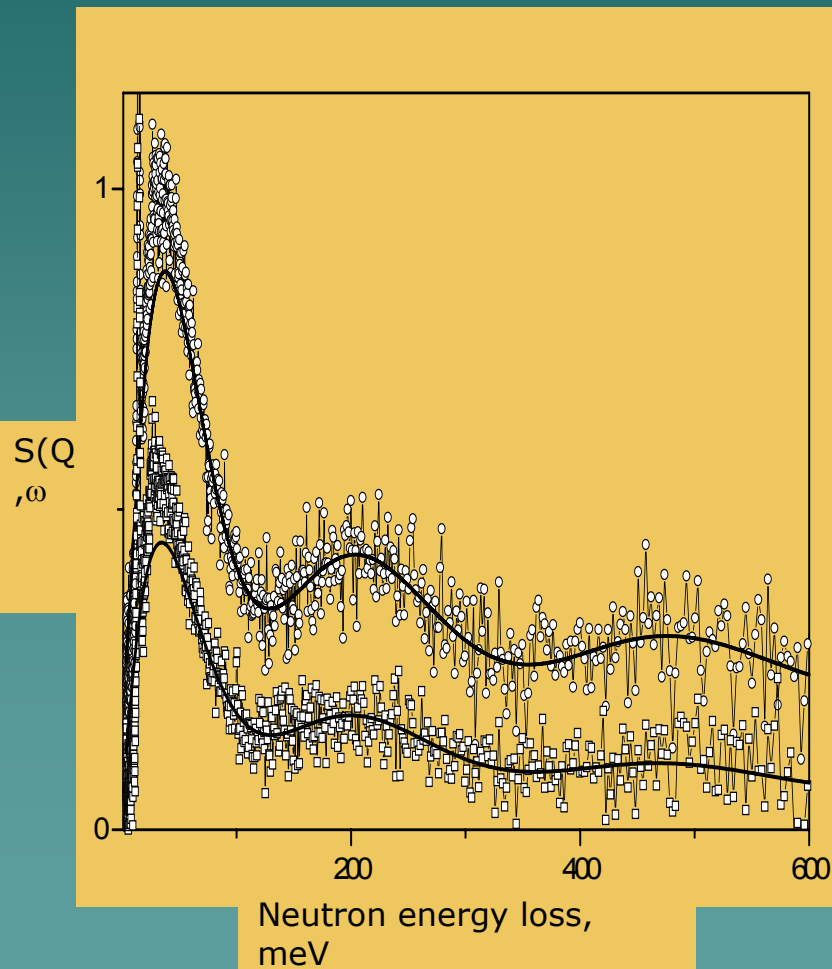
$F_{Jm, J'm'}(Q)$ is the Form Factor for the transition

$S_{CM}(Q, \omega)$ is the Scattering Function for the Centre of Mass motion in the potential energy surface seen by the molecule

For a bound atom, this consists of a delta function modified by the Debye-Waller factor for the molecule and an inelastic part – which for large Q becomes like the Perfect Gas Law but with a higher temperature

(a) Fits to the recoil spectra for 100% and 144% surface coverage using γ and K between 85 and 500 meV

(b) Plot of fitted temperature versus surface coverage



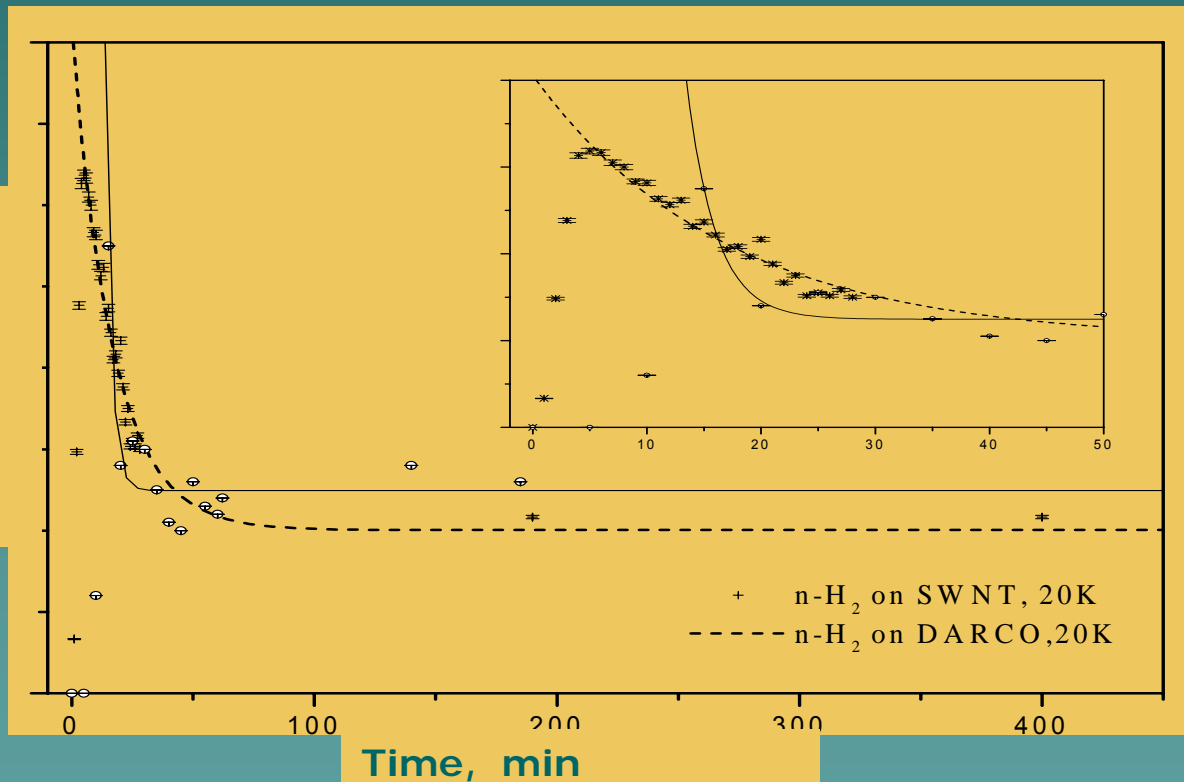
Ortho-Para Transition rate

- Only get measurable elastic scattering from Ortho
- Fill sample with ambient gas and observe elastic scattering during conversion process, looking for quasi-elastic scattering using IRIS
- Conversion is too fast to see any QE but we observe the conversion rate on SWNTs – suggests H_2 sees magnetic field.
- Catalyst particles are covered with amorphous carbon so suggests that they may have some magnetic properties

Integrated Elastic Intensity as a function of time after introducing warm gas

- ◆ *Half life SWNT 3 min*
- ◆ *Half life DARCO Activated carbon 16 min*

EISF,
arb.
units



Conclusions

- ◆ Neutron Scattering gives very direct information about the behaviour of hydrogen in storage materials that enables us to understand what is happening and hence to design improved materials